AD-769 986

CONCERNING THE EFFECT OF THE NATURE OF THE COMBUSTIBLE AND THE CATALYTIC AGENTS ON THE COMBUSTION OF AMMONIUM AND POTASSIUM PERCHLORATE BASED MIXTURES

A. P. Glazkova, et al

Foreign Technology Division
Wright-Patterson Air Force Base, Ohio

6 November 1973

FTD-HT-23-629-74

FOREIGN TECHNOLOGY DIVISION

CONCERNING THE EFFECT OF THE NATURE OF THE COMBUSTIBLE AND THE CATALYTIC AGENTS ON THE COMBUSTION OF AMMONIUM AND POTASSIUM PERCHLORATE BASED MIXTURES

by

A. P. Glazkova, O. K. Andreyev

Approved for public release; distribution unlimited.

Unclassified
Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author) Foreign Technology Division Air Force Systems Command U. S. Air Force	2a. REPORT SECURITY CLASSIFICATION Unclassified 2b. GROUP

3. REPORT TITLE Concerning the Effect of the Nature of the Combustible and the Catalytic Agents on the Combustion of Ammonium and Potassium Perchlorate Based Mixtures

4. DESCRIPTIVE NOTES (Type of report and inclusive dates)
Translation

5. AUTHOR(S) (First name, middle initial, last name)
A. P. Glazkova, O. K. Andreyev

6. REPORT DATE	7a. TOTAL NO. OF PAGES	7b. NO. OF REFS
1972	7 /2	10

8a. CONTRACT OR GRANT NO. b. PROJECT NO. AP5C, AP5E c. d.	9a. ORIGINATOR'S REPORT NUMBER(S) FTD-HT-23-629-74 9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)

10. DISTRIBUTION STATEMENT
Approved for public release; distribution unlimited.

11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY
	Foreign Technology Division Wright-Patterson AFB, Ohio

13. ABSTRACT
20

ia

DD FORM 1 NOV 65 1473

9/

Unclassified
Security Classification

FTD-HT- 23-629-74

EDITED TRANSLATION

FTD-HT-23-629-74 . 6 November 1973

CONCERNING THE EFFECT OF THE NATURE OF THE COMBUSTIBLE AND THE CATALYTIC AGENTS ON THE COMBUSTION OF AMMONIUM AND POTASSIUM PERCHLORATE BASED MIXTURES

By: A. P. Glazkova, O. K. Andreyev

English pages: 7

Source: Goreniye i Vzryv, 1972, pp. 78-82

Country of Origin: USSR

Translated by: Joseph E. Pearson

Requester: FTD/PDTA/G. W. Roberts

PREPARED BY:

TRANSLATION DIVISION
FOREIGN TECHNOLOGY DIVISION
WP-AFB, OHIO.

All figures, graphs, tables, equations, etc. merged into this translation were extracted from the best quality copy available.

U. S. BOARD ON GEOGRAPHIC NAMES TRANSLITERATION SYSTEM

Block	Italic	Transliteration	Block	Italic	Transliteration
А а	*А а*	A, a	Р р	*Р р*	R, r
Б б	*Б б*	B, b	С с	*С с*	S, s
В в	*В в*	V, v	Т т	*Т т*	T, t
Г г	*Г г*	G, g	У у	*У у*	U, u
Д д	*Д д*	D, d	Ф ф	*Ф ф*	F, f
Е е	*Е е*	Ye, ye; E, e*	Х х	*Х х*	Kh, kh
Ж ж	*Ж ж*	Zh, zh	Ц ц	*Ц ц*	Ts, ts
З з	*З з*	Z, z	Ч ч	*Ч ч*	Ch, ch
И и	*И и*	I, i	Ш ш	*Ш ш*	Sh, sh
Й й	*Й й*	Y, y	Щ щ	*Щ щ*	Shch, shch
К к	*К к*	K, k	Ъ ъ	*Ъ ъ*	"
Л л	*Л л*	L, l	Ы ы	*Ы ы*	Y, y
М м	*М м*	M, m	Ь ь	*Ь ь*	'
Н н	*Н н*	N, n	Э э	*Э э*	E, e
О о	*О о*	O, o	Ю ю	*Ю ю*	Yu, yu
П п	*П п*	P, p	Я я	*Я я*	Ya, ya

* ye initially, after vowels, and after ъ, ь; e elsewhere. When written as ё in Russian, transliterate as yё or ё. The use of diacritical marks is preferred, but such marks may be omitted when expediency dictates.

CONCERNING THE EFFECT OF THE NATURE OF THE COMBUSTIBLE AND THE CATALYTIC AGENTS ON THE COMBUSTION OF AMMONIUM AND POTASSIUM PERCHLORATE BASED MIXTURES

A. P. Glazkova and O. K. Andreyev
Moscow

It is known, that at low pressures potassium perchlorate based mixtures burn at higher rates than ammonium perchlorate based mixtures. This can be due to at least three reasons: the catalytic effect of the potassium [1], the formation of a liquid layer during combustion due to the fusion of KCl [2] and, finally, by the fact that in the decomposition of $KClO_4$, as is known from the data of literature [3], an oxygen-oxidizer is immediately formed, whereas in the decomposition of NH_4ClO_4 dual dissociation must occur for the formation of the oxidizer: of the perchlorate into ammonia and perchloric acid and of the latter into chlorine oxide and hydroxyl.

One of the possibilities for explaining the combustion mechanism of these mixtures consists in comparing the effect of the chemical nature of the oxidizer and the combustible on the combustion rate. It is also interesting to examine to what extent it is possible to affect the oxidation process during combustion by the addition of catalytic agents. According to the data of [4]

chlorine oxides do not react with ammonia at normal temperatures, but upon the addition of methane to ammonia they react right away with it.

In the present work substances were selected as combustibles, which do not contain carbon in their molecule and which yield ammonia (ammonium chloride) as the primary decomposition product; with a small carbon content which form ammonia (ammonium oxalate) upon their decomposition, and which do not form it (urea); the hydrocarbons - naphthalene, paraffin, o-phenylenediamine and, finally, pure carbon - carbon black. Stoichiometric mixtures with particle dimensions <250 μm were studied and catalytic agents[1] were added in an amount of 5%. The experiments were carried out in a constant pressure bomb [5]. The lower combustion limit with respect to pressure and the dependence of combustion rate on pressure in the range up to 1000 at were determined. As the criterion of the effectiveness of the catalytic agent effect coefficient Z_M was adopted, which was equal to the ratio of the mass combustion rate of the catalyzed mixture to the combustion rate of the mixture without the catalytic agent under the same conditions.

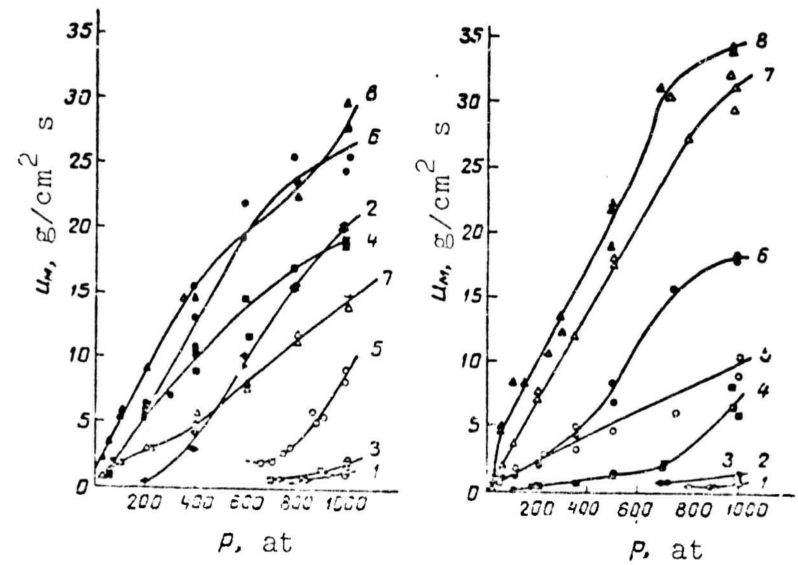
The experiments showed,[2] that the combustibles which yield ammonia (ammonium chloride, ammonium oxalate) upon decomposition, are poorly oxidized both by the decomposition products of perchloric acid, and also by oxygen. The lower limit of combustion for these mixtures is extremely high and under the conditions of our experiments (the diameter of the samples was 7 mm) was for mixtures based on NH_4ClO_4 700 at, and for mixtures based on $KClO_4$ 800 and 1000 at,

---

[1]The particle dimensions of the inorganic catalytic agents did not exceed 100 μm, the organic catalytic agents were in the finely dispersed state.

[2]The points on the curves represent the average values of 2-3 parallel experiments.

but even at 1000 at the mixtures burnt at extremely low rates ~1 $g/cm^2 \cdot s$. It is interesting to note, that the appearance of carbon in a molecule of combustible for mixtures based on NH_4ClO_4 stimulated the combustion process. Thus, a mixture with ammonium oxalate burnt approximately twice as fast as a mixture with ammonium chloride. The stimulating effect of small quantities of carbon for combustibles which do not yield ammonia upon decomposition manifests itself even more vigorously - in mixtures with urea.



The effect of copper oxinate on the combustion of mixtures based on NH_4ClO_4 (a) and $KClO_4$ (b). The sketched points pertain to catalyzed mixtures: 1, 2 - with NH_4Cl; 3, 4 - with ammonium oxalate; 5, 6 - with urea; 7, 8 - with o-phenylenediamine.

Mixtures based on $KClO_4$ burn at higher rates; a mixture with paraffin yields the maximum combustion rate; a mixture with naphthalene burns more slowly and a mixture with carbon black burns even more slowly. For mixtures based on NH_4ClO_4 the sequence of the arrangement of combustibles in the order decrease in rate varies somewhat (table). It is interesting to note, that,

The effect of catalytic agents (5%) on the combustion characteristics of stoichiometric mixtures based on ammonium and potassium perchlorates.

Combustible	Catalytic agent	NH_4ClO_4			$KClO_4$		
		B	ν	p, at	B	ν	p, at
NH_4Cl	None	$<10^{-5}$	~4,0	700–1000	$<10^{-5}$	4,53	800–1000
	Copper oxinate	0,00009	1,78	300–1000	—	—	—
$(NH_4)_2C_2O_4$	None	$<10^{-5}$	~1,24	800–1000	—	—	—
	Copper oxinate	0,082	0,786	100–1000	—	—	—
NH_2CONH_2	None	$1\cdot10^{-10}$	3,7	670–1000	0,019	0,762	50–1000
	$Cu_2Cr_2O_7\cdot2H_2O$	0,09 0,0004	0,667 1,73	20–200 400–1000	—	—	—
	Copper oxinate	0,031	0,97	200–1000	0,09 0,0025	0,61 1,30	50–200 200–1000
Carbon black	None	0,022	0,93	50–1000	0,14	0,637	10–1000
	Sulfur	0,065	0,76	50–500	0,09	0,71	30–1000
	$Cu_2Cr_2O_7\cdot2H_2O$	—	—	—	0,52 0,98	0,372 0,528	50–200 500–1000
	Fe_2O_3	—	—	—	0,40 0,038	0,45 0,837	50–300 400–1000
$C_6H_4(NH_2)_2$	None	0,11 0.0105	0,604 1,04	20–200 200–1000	0,08	0,87	10–1000
	Copper oxinate	0,185	0,732	200–1000	0,074	0,875	50–1000
$HOC_6H_4CO_2NH_3$	None	—	—	—	0,088 0,088	0,766 0,80	30–400 400–1000
	$Cu_2Cr_2O_7\cdot2H_2O$	—	—	—	0,049	0,86	50–1000
	Fe_2O_3	—	—	—	0,019	0,86	30–1000
$C_{10}H_8$	None	0,086 0,00086	0,616 1,40	10–400 400–1000	0,02	1,095	25–900
Paraffin	None	0,092	0,752	10–1000	0,01	1,23	25–1000

for example, at 1000 at a mixture of NH_4ClO_4 with NH_4Cl burnt 13 times more slowly, with ammonium oxalate - 8 times more slowly, and with urea - 2 times more slowly than ammonium perchlorate itself.

As the catalytic agents for the investigated mixtures inorganic [6] and organic [7] copper compounds were selected, which most effectively catalyze the combustion of ammonium perchlorate. On the figure data is represented with respect to the combustion of catalyzed mixtures, from which it is evident, that the effect of catalytic agents is much more significantly manifested for mixtures based on NH_4ClO_4. Thus, a mixture with ammonium chloride and copper oxinate began to burn at 200 at instead of 700 and at 1000 at burned 18 times faster than the pure mixture. The presence of a catalytic agent was even more strongly expressed at the lower limit for a mixture with ammonium oxalate - it dropped from 700 to 50 at, and the coefficient Z_M at 1000 at was equal to 10. For a mixture of ammonium perchlorate with urea the l er limit was ~200 at, and the combustion rate at 1000 at exceeded by 4 times the combustion rate of the uncatalyzed mixture. Even greater catalytic effects were observed with a reduction in pressure, since, at 800 at the combustion rate of mixtures with ammonium oxalate and NH_4Cl increased by 30 times.

For mixtures based on $KClO_4$ and NH_4Cl catalyzed with copper oxinate the lower limit dropped only by 100 at, the combustion rate at 1000 at did not vary; for a mixture with ammonium oxalate the lower limit dropped from 1000 to 700 at, and the combustion rate at 1000 at increased by 9 times and, finally, for mixtures with urea the lower limit dropped almost to atmospheric pressure, and the combustion rate at pressures above 400 at exceeded the combustion rate of the pure mixture by two times.

Thus, the pattern varies sharply for catalyzed mixtures: with one and the same combustible ammonium perchlorate based mixtures

burn at considerably greater rates. These results are in agreement with the data of literature, obtained for low pressures, in accordance with which compositions based on $KClO_4$ are catalyzed much less than those based on NH_4ClO_4 [8], and confirm the earlier made observations concerning the fact, that catalytic effects most strongly manifest themselves for slowly burning mixtures. However, the fact, that mixtures based on $KClO_4$, which even burn slowly, are catalyzed much more weakly than analogous mixtures bases on NH_4ClO_4, can attest not only to the fact, that catalysis already occurred with an ion or with potassium oxide, but also to the fact, that the role of the catalytic agent consists, apparently, in the liberation of elementary oxygen from the oxides. In the case of $KClO_4$, as was already noted above, the oxygen is liberated more simply.

The table sums up the obtained results and presents the values of B and ν in the combustion equation $u_M = Bp^{\nu}$. Let us note, that the presence of ammonia in a molecule of an organic compound (ammonium salicylate) is not reflected on the combustion rates - the curves for mixtures of potassium perchlorate with ammonium salicylate and salicylic acid coincide.

It is interesting to note, that the addition of a catalytic agent to a mixture of ammonium perchlorate with coke led to the fact, that the mixture burnt at the same rate as pure ammonium perchlorate with a catalytic agent [9], and mixtures of potassium perchlorate with carbon black and a catalytic agent (copper dichromate dihydrate, ferric oxide), as is apparent from the table, burnt in the pressure range up to 800 at at the same rate as uncatalyzed mixtures, and at high pressures the catalytic agents even reduced the combustion rate (by 20-30%). Let us dwell, finally, on mixtures of investigated oxidizers with o-phenylenediamine. The latter oxidizes readily and it was natural to expect, that mixtures with it will burn at the greatest rate. Experiments have shown, however, that o-phenylenediamine does not oxidize as well upon

burning as paraffin, both in the case, when NH_4ClO_4 is the oxidizer, as well in the case when $KClO_4$ is the oxidizer. At the same time it is known, that with the presence of perchloric acid in a molecule of o-phenylenediamine itself [10] the latter burns at the greatest rate of all the investigated organic perchlorates.

In conclusion, let us examine how the coefficients B and the exponent ν vary for the investigated mixtures. It is evident from the table, that, as a rule, coefficient B is greater for $KClO_4$ based mixtures than for analogous NH_4ClO_4 based mixtures, and the introduction into the composition of additives, which increase the combustion rate, leads to an increase in coefficient B, which attests to the fact, that the greater combustion rate of mixtures, where $KClO_4$ is the oxidizer, and also of catalyzed mixtures is due to the greater completeness of reaction occurrence in the condensed phase.

It is evident from what has been stated above, that the greatest effect of catalytic agents is observed, when NH_4ClO_4 is the oxidizer, and the combustible - compounds which yield ammonia upon decomposition. For similar types of mixtures extremely high catalytic effects were obtained for the first time - an increase in combustion rate by tens of times and a reduction in the lower combustion limit with respect to pressure by hundreds of atmospheres.

BIBLIOGRAPHY

1. К. К. Андреев. Термическое разложение и горение взрывчатых веществ. М., «Наука», 1966, стр. 151.
2. А. П. Глазкова, Ж. физ. хим., 1960, 37, № 5, стр. 1119.
3. C. E. Otto, H. S. Fry. J. Amer. Chem. Soc., 1923, 45, p. 1134.
4. I. Combourieu, R. Moreau, G. Moreau. C. r. Acad. sci., Paris, 1969, serie c, 269, p. 948.
5. А. П. Глазкова, П. А. Терешкин. Ж. физ. хим., 1961, 35, № 7, стр. 1622.
6. A. P. Glaskova. XIII Symp. (Internat.) on Combustion. Abstracts. Pittsburg, Pennsylvania, 1970, p. 161.
7. А. П. Глазкова, В. К. Боболев. Докл. АН СССР, 1971, 197, № 4, стр. 883.
8. C. U. Pittman, Jr. AIAA-j., 1969, 7, No 2, p. 328.
9. А. П. Глазкова. Физ. гор. и взрыва, 1966, № 1, стр. 59.
10. А. Е. Фогельзанг, Б. С. Светлов, В. Д. Алешин, В. С. Опрышко. В сб.: «II Всесоюзный симпозиум по горению и взрыву (Авторефераты докладов)». Черноголовка, 1969, стр. 32.